Institute of Paper Science and Technology

THE FEASIBILITY OF THERMAL DESTRUCTION OF CHLORINE-CONTAINING CONCENTRATED STREAMS FROM CLOSED CYCLE PROCESSES

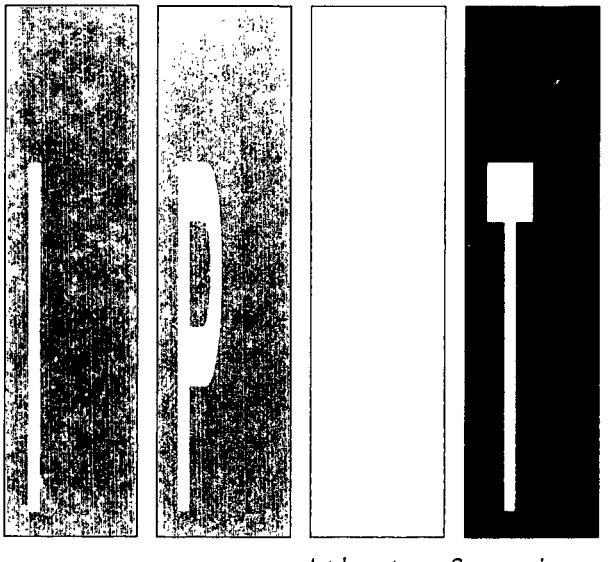
Project 3671

Final Report

to the

National Council of the Paper Industry for Air and Stream Improvement

December 1, 1990



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Final Report

THE FEASIBILITY OF THERMAL DESTRUCTION OF CHLORINE-CONTAINING CONCENTRATED STREAMS FROM CLOSED CYCLE PROCESSES

IPST Project No. 3671

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For The National Council of the Paper Industry for
Air and Stream Improvement

December 1, 1990

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THE FEASIBILITY OF THERMAL DESTRUCTION OF CHLORINE-CONTAINING CONCENTRATED STREAMS FROM CLOSED CYCLE PROCESSES

1. EXECUTIVE SUMMARY

The objective of this study has been to evaluate the feasibility of incinerating chlorine-containing concentrates from bleach plant effluents. Efforts during this reporting period have focused primarily on gathering and interpretation of data on the chemical composition and physical properties of concentrated streams, and data on the combustion behavior (i.e., burning rates, fate of chlorine, ash characteristics) of concentrated streams.

Using laboratory-scale filtration equipment, samples of chlorine-containing concentrates from closed cycle processes were obtained. Four mill effluents were treated with ultrafiltration (UF) and with reverse osmosis (RO), giving eight samples of concentrated streams. Filtration flux rates, removal efficiencies, and concentrate solids levels were representative of values reported for previous laboratory and pilot scale ultrafiltration of bleach plant effluents.

The UF treatment tended to be selective in removal efficiencies, yielding a higher level of organics in the concentrates compared to inorganics levels. This resulted in UF concentrates having higher levels of carbon, organic-to-inorganic ratio, and heating value, and lower levels of ash than RO concentrates. These factors make the RO concentrates less desirable as a fuel. The compositions of UF concentrates were found to be similar to black liquor solids, with the notable exception of higher chlorine levels. Heating values of UF concentrates were similar to or higher than heating values for black liquor solids. Molar ratios of Na to Cl showed an excess of Cl for concentrates of C/D effluents and an excess of Na for concentrates of E1 effluents.

Densities of the concentrated streams were dependent primarily on weight percent solids and temperature. Significant differences in density were not seen among differences in mill (Mill A versus Mill B), bleach stage (C/D versus E1), and treatment (UF versus RO). A two-parameter equation can thus predict the density of the concentrated streams based on a knowledge of the solids and the temperature, to within an accuracy of the experimental error for measuring these two parameters. The density characteristics of the concentrated streams were found to be nearly identical to the density characteristics of black liquor solids.

Viscosities correlated well with percent solids and temperature for individual streams, but varied dramatically among streams. Two streams, at similar levels of solids and temperature, yielded viscosities which differed by greater

than a factor of ten. Thus, a single correlation cannot adequately describe viscosity for a variety of concentrated streams. Viscosity must be characterized for each stream unless estimates are needed only to an order of magnitude accuracy.

Nonisothermal burning data (TGA) in air and in argon showed that UF concentrates of E1 effluent contain approximately 80 weight % combustibles, and 20% non-combustible ash (primarily NaCl). The combustibles are approximately one-half volatiles. These evolve in the temperature range of 200-600 °C. The non-volatile char is oxidized in air via heterogeneous reactions in the temperature range of 600-900 °C.

Isothermal mass loss data in air provided information on burning rates of UF/E1 concentrates at 700 and 800 °C. The mass loss data are predicted very well by a two-part model, consisting of one rate expression for devolatilization which is first-order in volatiles concentration, and a second rate expression for char burning which is first-order in char and oxygen concentrations. Activation energies derived from the isothermal data show that at 700 °C the rate of devolatilization doubles with a temperature rise of 150 °C, and the rate of char burning doubles with a temperature rise of 80 °C.

The fate of chlorine was shown to be heavily dependent on the relative proportion of sodium. Upon heating (at 700 °C in air) of UF/E1 concentrates which had Na/Cl molar ratios of 1.5-2.3, the level of organic chlorine in the unburned residue decreased. This decrease was mirrored by a commensurate increase in organic Cl found in the unburned residue. The organic chlorine did not evolve as gaseous chlorine-containing species, but was trapped in the solid residue as NaCl. This trapping occurred during devolatilization at a rate 2-5 times that of devolatilization. This is a significant result since it implies minimal emissions of trace levels of PCDD/PCDF and other chlorinated organics during concentrate burning.

The non-combustible ash consisted primarily of NaCl, with lesser amounts of Na_2SO_4 and very little Na_2CO_3. The ashes showed initial deformation at temperatures of 700-790 °C and complete melting at temperatures of 840-1050 °C. Levels of Na and Cl in ash samples verified that organic chlorine was quantitatively trapped for concentrates of E1 effluent which contained excess Na, while it was not trapped for concentrates of C/D effluent which contained excess Cl.

On consideration of these various results, it was concluded that feasibility is high for thermal destruction of UF concentrates of E1 effluents, while feasibility is much less for thermal destruction of other concentrates. Fluidized bed combustion appears to be the most attractive thermal destruction technology for these concentrates because it will provide for effective organics destruction at temperatures sufficiently low that the non-

combustible ash will remain in the solid phase (i.e., will not melt). Future work is recommended to evaluate the potential of fluidized bed technology for combustion of chlorine containing concentrates.

Since the chemical composition, heating value, and physical properties of UF concentrates are similar to kraft black liquor, it may be feasible to add these concentrates to black liquor and burn the mixture in a recovery furnace. The reasonably low levels of chlorine in concentrate solids (8-9 weight %) may not result in chloride levels in the recovery cycle which are higher than levels experienced routinely at coastal mills. Future work is recommended to evaluate the feasibility for burning concentrates in recovery furnaces.

2. BACKGROUND AND OBJECTIVES

There is a potential that existing bleached kraft mills will move toward closed cycle technologies. A number of these closed cycle technologies, such as ultrafiltration, polymer treatment, resin treatment, and activated carbon treatment, would produce concentrated effluent streams that may contain high concentrations of lignin, chlorinated organics, and inorganic chlorides. These streams would have to be treated either through recycling within the process or in a separate treatment system. At present the only demonstrated technology for treating these concentrated streams is through concentration in multiple-effect evaporators, followed by burning in the recovery furnace. A potentially serious adverse impact of burning these concentrated streams in the recovery furnace is increased chloride in various process streams.

The general behavior of such streams in a kraft recovery boiler is reasonably well understood. The chlorocompounds are converted to NaCl. In regions of the furnace where there is a molar excess of sulfur over sodium, HCl gas can be released. The NaCl produced will form low-melting eutectics with the other furnace ash constituents (Na_2CO_3 and Na_2SO_4), and this can cause serious problems with fouling and corrosion in the convective passages of the recovery boiler. The chloride produced remains in the recovery cycle, often requiring elaborate chloride-purge technologies to prevent build-up of very high levels of chloride.

Because of these concerns very few facilities are likely to implement closed cycle technologies that require the burning of concentrated streams in the recovery furnace. Consequently, if alternative technologies are developed to effectively and economically treat the concentrated streams from closed cycle processes, these closed cycle technologies will more likely be implemented at bleached kraft mills.

The feasibility of any thermal destruction approach depends on many issues including the chlorocompound destruction efficiency, the nature of the gaseous products, and the phase-behavior of the resultant ash. Thermal destruction of streams containing C, H, O, Na, and Cl will produce NaCl, HCl, and Na_2CO_3, respectively, depending on the proportion of Na and Cl in the process stream. Combustion of these streams raises a question concerning the degree of destruction of chlorinated organics and the possibility that undesirable compounds may be formed as intermediates during the combustion process. Adding other elements, such as Mg or C, into the process streams or as part of the combustion process could complicate this behavior, since it is not clear how these elements affect the resulting fate of the chlorine.

The objective of this study has been to evaluate the feasibility of thermal destruction of chlorine-containing concentrated streams from closed cycle

processes in a device other than the kraft recovery furnace. This was accomplished primarily by characterizing the chemical composition and physical properties of simulated closed cycle streams, as well as their combustion behavior (burning rate, fate of chlorine, and ash behavior).

3. CHARACTERIZATION OF THE CLOSED CYCLE CONCENTRATES

In order to conduct laboratory testing for the characterization of concentrates, it was necessary to have samples of these concentrates. It was not possible to obtain samples from industry, since closed cycle technologies are not presently being applied in the pulp and paper industry. To overcome this problem, the decision was made to simulate the concentrates in the laboratory. This was done by obtaining a limited number of samples of bleach plant effluents (C/D and E1) from kraft pulp mills, and treating these effluents at IPST using laboratory-scale closed cycle technologies to produce enough concentrates for characterization and combustion testing. The closed cycle technologies selected for laboratory-scale treatment were ultrafiltration (UF) and reverse osmosis (RO).

3.1 Description of Laboratory-Scale Filtration

The laboratory-scale treatment was accomplished using the plate-and-frame filtration equipment shown in Figure 3.1-1. The filtration module was a LAB 20 unit of DDS (De Danske Sukkerfabrikker, Nakskov, Denmark), equipped with a vertical stack of membrane support plates that were situated between spacers. The total membrane surface area was 0.72 m^2 (7.8 ft^2). A hydraulic cylinder, which was pressurized using a hand pump, was in the base of the filtration module to maintain a compression force on the membrane stack.

The filtration was performed batchwise. The feed was initially charged to the feed tank. The high-pressure pump delivered the feed from the feed tank to the filtration model at the desired operating pressure. The operating pressure was defined as the average of the pressure at the module inlet and the pressure at the module outlet. The permeate (liquid which passed through the membrane) was collected. The concentrate (liquid which did not pass through membrane) was returned to the feed tank. Filtration would continue in this manner until the volume of liquid in the feed tank had decreased to the desired concentration factor (defined as initial feed volume divided by final feed volume). This same batchwise procedure was used for both the UF and RO, the only difference being the operating pressure and the membrane type.

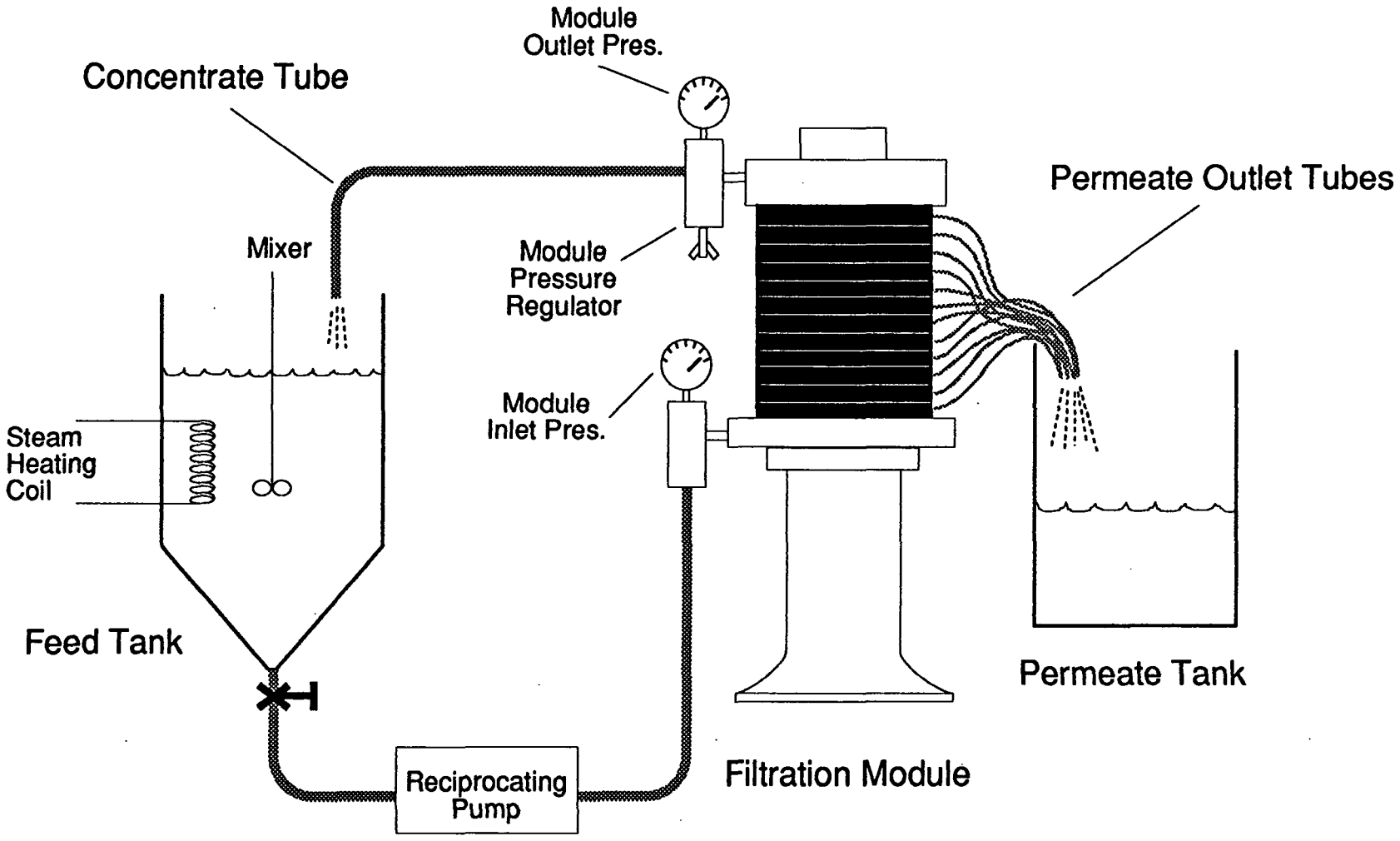

Figure 3.1-1. Schematic of Laboratory-Scale Filtration Equipment.

Operating pressure, temperature, concentration factor, and membrane type for UF were chosen based on typical operating conditions used for the pilot-scale UF demonstration performed at Champion's Canton Mill (Champion International Corporation, 1986). These were a pressure of 1.0 MPa (10 atm), a temperature of 60 °C (140 °F), a concentration factor of 40 (80 liter initial feed volume, 2 liter final feed or concentrate volume), and DDS GR-81PP membranes. These are polysulfone membranes on polypropylene backing with a molecular weight cutoff of 6,000. The same operating conditions were used for RO, except that operating pressure was 4.0 MPa (40 atm) and the membranes were DDS HR-95PP. These membranes are a thin film composite membrane with a polyamide surface coating on a polysulfone substrate and a polypropylene backing, and give a 95% salt retention based on 2000 ppm NaCl. Cleaning of the filtration equipment was performed by circulating 0.5 weight % NaOH for the UF membranes and 0.5 weight HNO_3 for the RO membranes.

Filtration flux rates decreased with time as a result of membrane fouling and increasing feed concentration in the batchwise procedure. For both UF and RO, initial flux rates were in the range of 150-200 L/m^2h. Average flux rates were approximately 30 L/m^2h for UF and 20 L/m^2h for RO. Dorica, et al. (1986) reported much higher average flux rates (198 L/m^2h) for similar laboratory-scale batchwise UF of E-stage effluent. This large difference in flux rates may be explained by (1) differences in concentration factor and (2) differences in prefiltering. The concentration factor for Dorica, et al. was 16.2 (94.2% filtrate recovery) while the concentration factor in this study was 40. Dorica, et al. prefiltered the E effluent using a bag filter with a pore size of 1 micron. The effluents in this study were prefiltered using #13255 Cenco creped filter paper (size approximately 35 micron).

3.2 Chemical Composition of Concentrates

Using the equipment and procedures described above, four mill effluents (C/D and E1 effluents from Mills A and B) were treated with both UF and RO resulting in eight simulated concentrates. Chemical characteristics of the resulting concentrates are provided in Tables 3.2-1 through 3.2-4. The permeates were not of interest and therefore were not characterized. In mill operation the permeate liquor would be recycled for re-use in the mill. In general, the RO removed more of the total solids, (64-85%) than UF (12-50%), although UF removed color approximately as well as RO. The UF tended to be more effective for removing organic compounds. This is evidenced by much higher UF removal efficiencies for color, carbon, and organic chlorine than for sodium and inorganic chlorine.

TABLE 3.2-1. Filtration Results: Mill A C/D Effluent			
	Untreated	UF(X38)[a]	RO(X40)
Total Solids mg/L	2,690	12,300(12.0%)[b]	68,800(63.9%)
Color, C.U.	1,060	19,500(48.4%)	36,000(84.9%)
Total Organic Carbon, mg/L	461	3,900(22.3%)	9,320(50.5%)
Chlorine, mg/L	985	2,480(6.63%)	26,500(67.3%)
Organic Chlorine, mg/L	100	980(25.8%)	2,740(68.5%)
Sodium, mg/L	366	675(4.85%)	9,780(66.8%)
Sulfur, mg/L	32	226(18.6%)	764(59.7%)

[a] concentration factor, feed volume/concentrate volume

[b] percentage removal

TABLE 3.2-2. Filtration Results: Mill A E1 Effluent			
	Untreated	UF(X31)[a]	RO(X27)
Total Solids, mg/L	4,090	62,900(49.6%)[b]	92,800(84.0%)
Color, C.U.	14,800	386,000(84.1%)	334,000(83.6%)
Total Organic Carbon, mg/L	1,165	29,500(81.7%)	24,900(79.2%)
Chlorine, mg/L	953	5,770(19.5%)	14,300(55.6%)
Organic Chlorine, mg/L	104	1,300(40.3%)	2,130(10.7%)
Sodium, mg/L	736	5,490(24.1%)	19,200(96.6%)
Sulfur, mg/L	18.4	371(65.0%)	464(93.4%)

[a] concentration factor, feed volume/concentrate volume

[b] percentage removal

TABLE 3.2-3. Filtration Results: Mill B C/D Effluent			
	Untreated	UF(X40)[a]	RO(X39)
Total Solids, mg/L	1,390	10,700(19.2%)[b]	46,000(84.9%)
Color, C.U.	880	10,600(30.1%)	38,000(108%)
Total Organic Carbon, mg/L	384	2,580(16.8%)	7,250(48.4%)
Chlorine, mg/L	455	2,080(11.4%)	20,800(114%)
Organic Chlorine, mg/L	145	509(8.9%)	3,120(53.8%)
Sodium, mg/L	239	480(5.0%)	5,060(54.3%)
Sulfur, mg/L	32	311(24.3%)	1,044(83.7%)

[a] concentration factor, feed volume/concentrate volume

[b] percentage removal

TABLE 3.2-4. Filtration Results: Mill B E1 Effluent			
	Untreated	UF(X40)[a]	RO(X40)
Total Solids, mg/L	6,790	96,600(35.6%)[b]	160,000(58.9%)
Color, C.U.	18,800	569,000(75.7%)	490,000(65.2%)
Total Organic Carbon, mg/L	1,370	39,100(71.4%)	38,900(71.0%)
Chlorine, mg/L	1,980	7,500(9.5%)	33,200(41.9%)
Organic Chlorine, mg/L	809	782(2.4%)	3,504(10.8%)
Sodium, mg/L	1,900	11,000(14.0%)	42,900(54.7%)
Sulfur, mg/L	29	560(48.3%)	912(78.6%)

[a] concentration factor, feed volume/concentrate volume

[b] percentage removal

The level of solids in the concentrates is comparable to other ultrafiltration study results. For the two E1 concentrates from UF treatment (Tables 3.2-2 and 3.2-4) the total solids levels of 62.9 and 96.9 g/L are the equivalent of 6.1% and 9.2% solids, respectively. By comparison, Dorica (1986) reported total solids levels of 5.3% to 7.5% for pilot plant UF of E-stage effluents. Lundahl and Mansson (1980) reported total solids of 50 g/L from reference plant UF of 130,000 gal/day alkali-extraction stage effluent from softwood kraft bleaching. The one-year UF demonstration of E effluent by Champion at the Canton Mill yielded 8-10% total solids in the concentrate stream.

Elemental Composition

Table 3.2-5 shows the elemental composition of the concentrates on a moisture-free basis. The moisture was driven off, prior to elemental analyses, by heating at 105 °C. The sum of the values for the elements shown is, in some cases, less than 100%. In these cases semi-quantitative emission spectrographic analysis was performed, confirming that the balance consisted primarily of Ca and Mg.

The chemical composition of the UF concentrates is similar to the composition of black liquor solids (BLS), with the notable exception of Cl content, which is much higher (by a factor of ten or more) for the UF concentrates. This high Cl level makes processing of these streams in multiple effect evaporators and recovery furnaces a less than desirable proposition. The increased chloride content, if high enough, would result in decreased equipment life, exotic metal requirements, and the need for chloride purging equipment. This was demonstrated by the experience at Great Lakes Forest Product's mill in Thunder Bay, Ontario. Some of the difficulties experienced at this mill were severe corrosion of the recovery furnace superheater tubes, and shortened life of the recovery furnace and evaporator tubes. Trends toward higher pressure boilers would increase these concerns.

Levels of C, H, and O in the UF concentrates were very similar to typical BLS. The UF concentrates have less sodium, approximately one-half as much as the BLS. The ratios of organic-to-inorganic are also similar, with the UF concentrates showing a somewhat higher ratio than the BLS.

An important issue in the combustion of a fuel containing chlorine is the proportion of Na and Cl present in the fuel. Values are shown in Table 3.2-5 of the molar ratio of Na/Cl for each concentrate. These values indicate a molar excess of Cl for the concentrates from C/D effluents, and a molar excess

Table 3.2-5. Elemental Composition of Concentrates, Moisture Free Basis

	Mill A C/D		*Mill A E1*		*Mill B C/D*		*Mill B E1*		*Other Fuels*		
	UF	RO	UF	RO	UF	RO	UF	RO	BLS[a]	MSW[b]	Coal[c]
C (total)	33.5	15.7	47.9	30.5	32.2	18.12	42.4	24.4	39.0	34.2	77.7
C (carbonate)	0.03	0.02	0.18	0.47	0	0.03	0.24	0.73			
H	2.54	2.24	3.58	2.59	2.38	2.53	3.37	2.53	3.8	4.5	5.0
O	31.2	22.2	30.1	26.8	31.7	22.9	34.8	26.3	33.0	27.1	6.2
Cl (total)	20.1	38.6	9.17	22.7	19.4	45.3	7.76	20.8	0.6	0.7	
Cl (organic)	7.95	3.98	6.80	2.30	4.76	6.78	5.76	2.19			
Na	5.49	14.2	8.73	20.7	4.49	11.01	11.39	26.8	18.6		
K	0.26	0.73	0.04	0.13	0.50	1.47	0.06	0.15	1.2		
S	1.84	1.11	0.59	0.50	2.91	2.27	0.58	0.57	3.6	0.3	1.6
Other Inorganic									0.2	32.6	8.0
Na/Cl Molar Ratio	0.42	0.57	1.47	1.41	0.36	0.37	2.26	1.99	4.80		
Heating Value KJ/Kg[d]	12,400	4,300	19,200	11,600	12,000	5,560	15,300	8,480	15,400	10,400	32,300
Organic/ Inorganic Ratio	4.30	0.83	5.25	1.50	3.77	1.03	4.40	1.21	3.24	2.02	10.9

[a] Black Liquor Solids (Adams and Frederick, 1988)
[b] Municipal Solid Waste (Seeker, et al., 1987)
[c] Bituminous Coal (Reid, et al. 1973)
[d] Determined by Bomb Calorimeter

of Na for the concentrates from E1 effluents. These proportions suggest that with combustion of C/D concentrates, significant quantities of HCl would be produced/emitted, while combustion of E1 concentrates is expected to yield less HCl.

All of the concentrates contain significant levels of sulfur, from 0.5 to 2.9 weight %. Much of this sulfur will be released during combustion to form H_2S and/or SO_2. This could potentially result in unacceptable SO_2 levels. However, with significant Na present, most of this sulfur will be captured by Na as Na_2SO_4, similar to the recovery furnace process, where sulfur gases are captured by fume. This is especially true for the E1 concentrates which contain a molar excess of Na.

All of the concentrates were analyzed for N, but contained relatively small amounts (0.02-0.12 weight %). Considering that coals contain 1-2% N, the levels found in these concentrates will probably not yield a significant level of fuel-NO_x during combustion.

Heats of Combustion

Another important characteristic in evaluating the feasibility of combusting concentrated streams is the heating value, or the energy released from the exothermic combustion reactions. Heating values were determined for the concentrates using a bomb calorimeter and are reported in Table 3.2-5. Included in Table 3.2-5 are heating values of other fuels for comparison. The UF concentrates have heating values of 12,000-19,200 kJ/kg which are in the same range as a typical heating value for black liquor solids. This suggests the feasibility of burning these UF concentrates in conventional combustion equipment. Heating values for RO concentrates (4,300-11,600 kJ/kg) were significantly lower than UF concentrate heating values, and were on the average lower than the heating value for municipal solid wastes. This suggests that RO concentrates are a less desirable fuel than UF concentrates.

Most likely, the UF concentrates have higher heating values because the UF membranes preferentially reject compounds with higher molecular weights. Thus, UF concentrates contained higher levels of organics such as complex hydrocarbons and lower levels of inorganics such as NaCl than did the RO concentrates. This ratio of organic content to inorganic content affects the heating values, since the organics are the major contributor to the net heating value; the inorganics contribute little or nothing. This results in higher heating values for the UF concentrates.

As shown in Figure 3.2-1, the heating values correlate reasonably well with the organic/inorganic ratio. These values were determined by dividing the sum of weight fractions of the elements C, H, O, Organic-Cl, and S to the sum

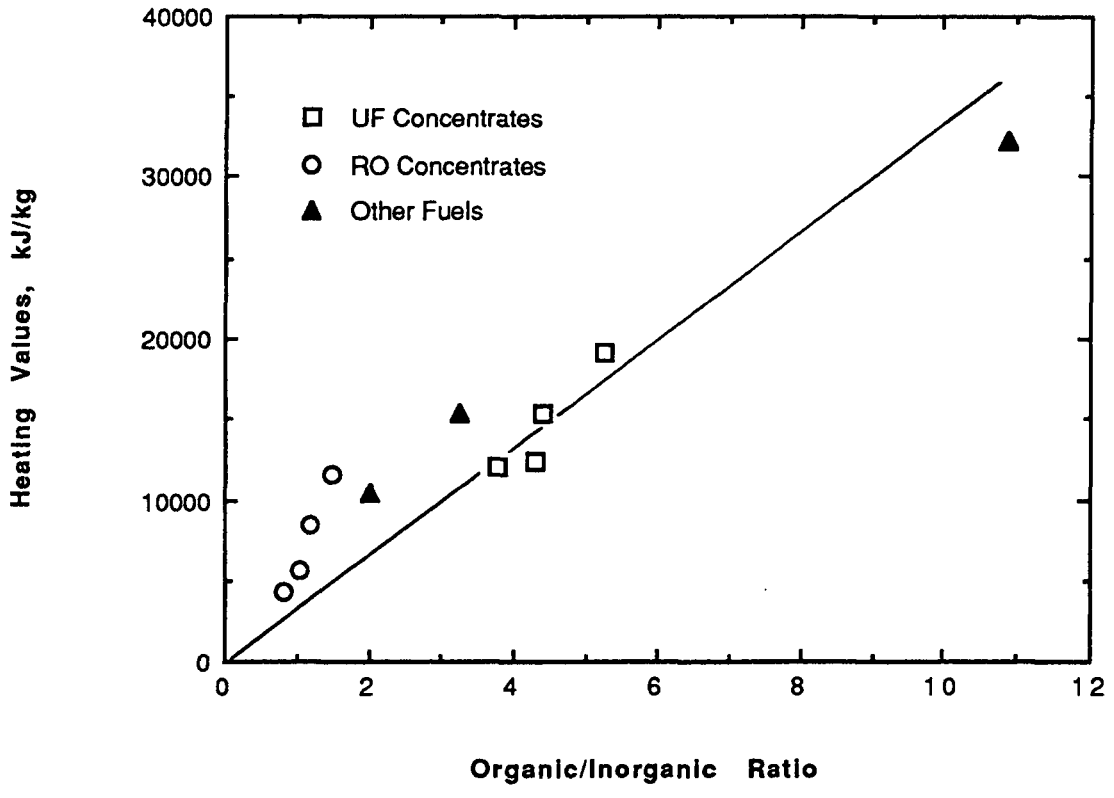

Figure 3.2-1. Higher heating values of the concentrates

of weight fractions of the elements Na, K, Inorganic-Cl, and other inorganics. A simple least squares fit of the data in Figure 2 gives the following relationship ($r^2 = 0.94$)

$$HV = 3260\ (O/I) \qquad \text{(eqn 3.2-1)}$$

where HV is the heating value in kJ/kg and O/I is the ratio of organics to inorganics. The assumption that all of the carbon content is organic carbon is supported by the carbonate-carbon weight fractions which are much smaller than the total-carbon weight fractions.

3.3 Physical Properties of Concentrates

Quantitative knowledge of physical properties is needed to make calculations and estimations of combustion phenomena such as heat transfer, mass transfer, and fluid dynamics. The properties generally of interest are specific gravity, viscosity, thermal conductivity, heat capacity, vapor pressure, and surface tension. The data and discussion in this report focus on specific gravity and viscosity.

Specific Gravity

The specific gravity characteristics for different concentrates were found to be very similar, as seen in Figure 3.3-1. Specific gravity was dependent primarily on solids level and temperature. There were no detectable differences in specific gravity when comparing C/D concentrates to E1 concentrates, or when comparing concentrates from Mill A to those of Mill B.

Specific gravity decreased with increasing temperature. This temperature effect is approximately linear with increasing temperature, although it appears to be more pronounced at the higher temperatures (80-100 °C). The increase in specific gravity with solids is also approximately linear. These two observations suggest that a single linear correlation will describe the specific gravity data. A least squares determination based on all of the data (both UF and RO) gives the following relation ($r^2 = 0.9796$)

$$sg = 1.008 + 0.0063\ (S) - 0.00042\ (T) \qquad \text{(eqn 3.3-1)}$$

where S is weight percent solids, and T is in degrees C. Equation 3.3-1 predicts values for specific gravity of the concentrates which are, in all cases, within 3.1% of the measured values.

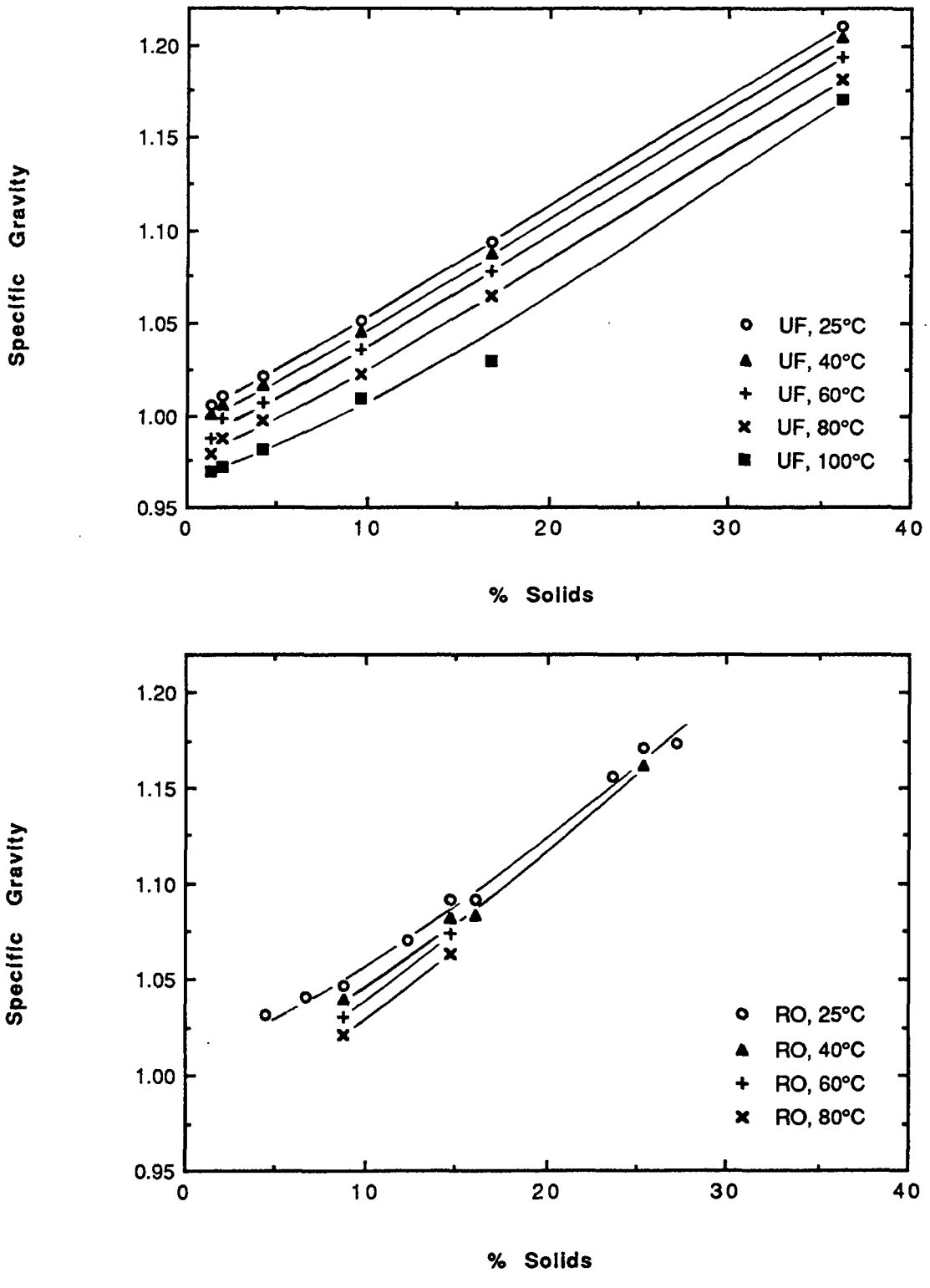

Figure 3.3-1. Specific gravity values of the concentrates

Venkatesh and Nguyen (1985) discuss the equation originally presented by Regestad (1951) relating the density of black liquor to temperature and concentration. This equation is

$$\text{Density, kg/m}^3 = 1007 + 6.0\,(S) - 0.495\,(T) \qquad \text{(eqn 3.3-2)}$$

The similarity of these two equations suggests that the density characteristics of bleach plant concentrates are similar to the density characteristics for black liquor. This is not surprising considering that the compositions of the concentrates and black liquor differ primarily only in the level of chlorine present.

There is a slight difference between specific gravity values for UF concentrates and for RO concentrates. Figure 3.3-2 shows specific gravity data for both at 25 °C. This slight difference can be explained by the differing relative amounts of inorganic present in the concentrates. Figure 3.3-2 includes specific gravity data for aqueous NaCl solutions (Wolf, et al. 1974). Specific gravity increases with decreasing ratios of organic-to-inorganic, the limiting case being aqueous NaCl for which this ratio is zero. As explained earlier, this difference resulted from the membrane differences. The UF membranes were more selective in rejection characteristics, and the efficiency for removing organics was higher than the efficiency for removing Na and Cl. Thus the UF concentrates tended to contain more organics and less Na and Cl on a relative basis than did RO concentrates.

Another data reduction scheme for specific gravity is that used by Fricke (1987) wherein the specific gravity data are considered in comparison to a reference state, as reduced specific gravity data. This is done by dividing the specific gravity (at any solids concentration) and temperature by the specific gravity of the same concentrate (at the same solids concentration) and 25 °C to determine the reduced specific gravity. Thus, by definition, reduced specific gravity is 1.000 at 25 °C for all concentrates. Using the data of Figure 3.3-2, values of reduced specific gravity were determined, and are plotted in Figure 3.3-3. As suggested by Fricke, this relation is fit with a second-order polynomial in temperature to give

$$sg_r = sg_T/sg_{25} = 1.003 - 5.30 \times 10^{-5}(T) - 3.69 \times 10^{-6}(T^2) \qquad \text{(eqn 3.3-3)}$$

To apply Equation 3.3-3 it is necessary to know the specific gravity of the concentrate at 25 °C. Using Equation 3.3-1 for values of sg_{25} and substituting these into equation 3.3-3 predicts values for specific gravity which are in all cases within 2.4% of the measured values. Correlating the data in this

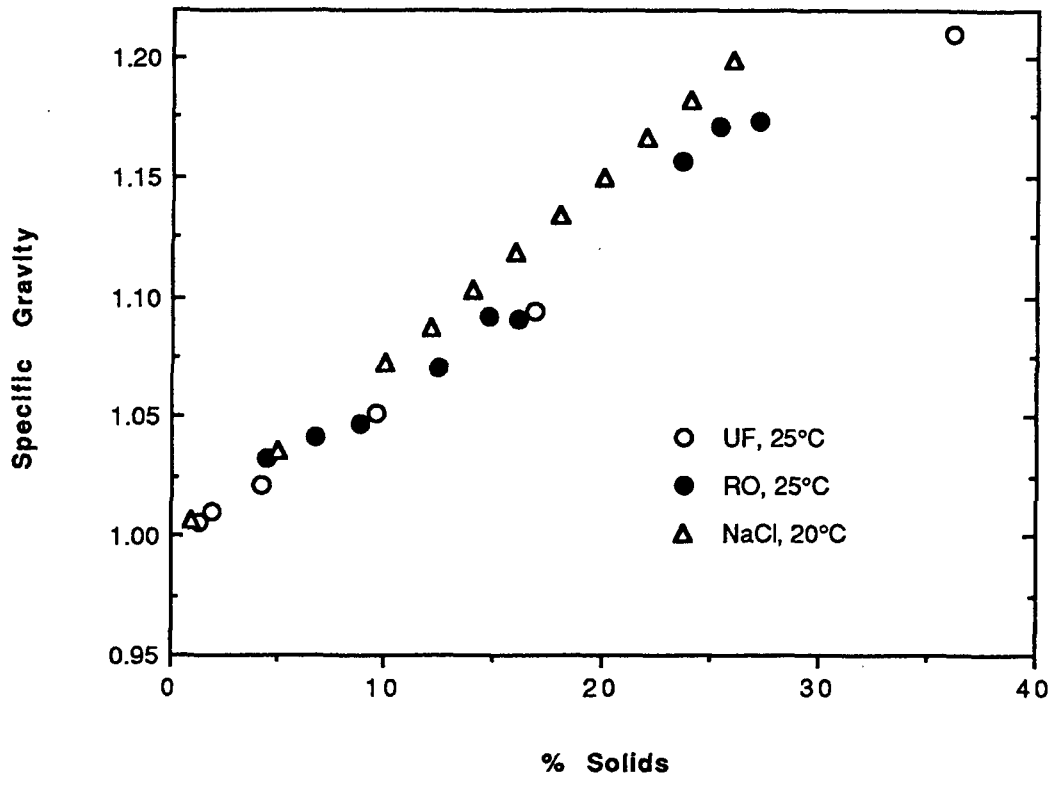

Figure 3.3-2. Comparison of specific gravity; UF versus RO concentrates

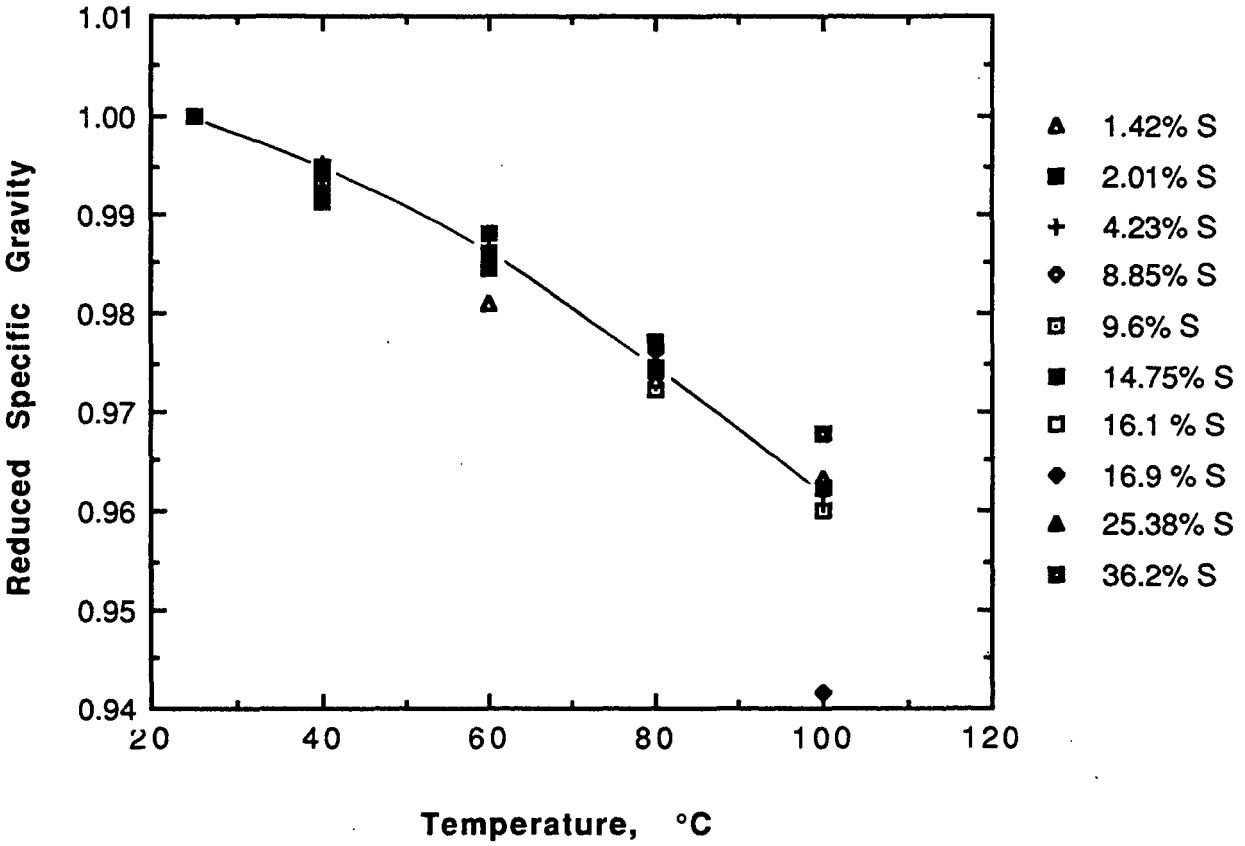

Figure 3.3-3. Reduced specific gravity of the concentrates

manner (as reduced specific gravity) has the advantage that it effectively separates most of the compositional effects (those related to solids level, chemical composition, pulp cooking conditions, etc.) from the temperature effects.

Summarizing, it is clear that specific gravity for the concentrated streams can be correlated by two variables, solids level and temperature, to an accuracy close to that of the experimental error for determining specific gravity. Specific gravity values were not significantly affected by changes in filtration technique (UF versus RO), bleaching stage (C/D versus E1), or mill (Mill A versus Mill B). This is similar to the conclusion of Fricke (1987) that specific gravity for black liquors does not vary significantly from one black liquor to another. Thus, the correlations above (Equations 3.3-1 and 3.3-3) are expected to predict, with reasonable accuracy, the specific gravity of bleach plant concentrates in the range 0-40% solids and 25-100 °C.

Viscosity

Viscosity determinations were made at five temperature levels (25, 40, 60, 80, 100 °C) and various solids levels (up to 40%) for each of the concentrates. No testing was performed to evaluate viscosity as a function of shear rate. It has been shown for black liquor that for solids levels up to 50%, viscosity does not depend on shear rate in the range of shear rates typical of mill operating conditions (Fricke, 1987; Adams & Frederick, 1988). As a result, black liquor is treated as a Newtonian fluid for process calculations. Given the similarities in chemical composition between black liquor and the concentrates of this study, it is assumed that there is no need to investigate non-Newtonian behavior of the concentrates.

The viscosity results for UF concentrates are shown in Figure 3.3-4 (viscosity was not determined for RO concentrates). In general, viscosity was found to increase with increasing solids, and to decrease with increasing temperature. Based on these observations, one might conclude that viscosity data could be correlated and a useful relation obtained showing the dependence of viscosity on solids and temperature. However, viscosities were found to vary by more than an order of magnitude among concentrates at similar conditions of solids and temperature. For example, Figure 3.3-4 shows that at 25 °C viscosity is over 1200 cP for E1 concentrate from Mill A at 29.3 % solids, while it is only 40 cP for E1 concentrate from Mill B at 36.2 % solids. The variation in viscosity among concentrates was much less for solids levels under 10 %.

These large differences are likely related to the effects of wood species and pulping conditions on lignin molecular weight. For example, greater chlorine doses would result in a greater breakdown of lignin and carbohydrate compounds in the effluent, yielding a lower average molecular

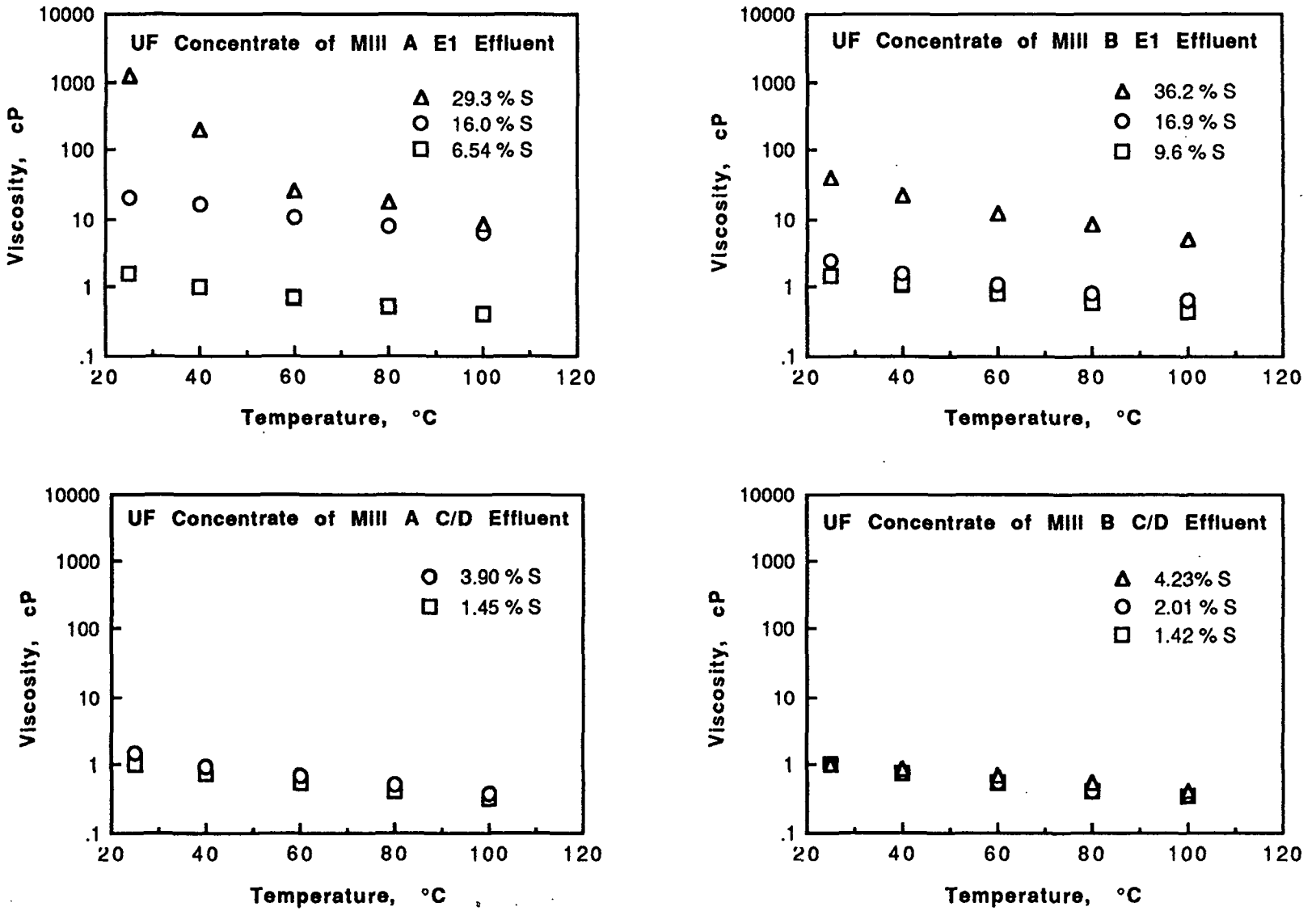

Figure 3.3-4. Viscosity values of UF concentrates

weight among the organics. Based on the viscosity characteristics of polymers, it is expected that a lower molecular weight would result in decreased viscosity for the concentrates. These differences become more dramatic at higher solids levels, because the organic phase plays a greater role in the resulting fluid rheology as solids level increases. This suggests that bleaching conditions will affect physical properties and thus must be considered in any burning scheme.

Similar variations are found among black liquor viscosity data. Adams & Frederick (1988) showed that black liquor samples from two mills, or from one mill at two different times, can have viscosities different by almost an order of magnitude at the same conditions of dry solids content and temperature. The implication of these data (Figure 3.3-4) is that a single correlation cannot adequately describe the viscosity characteristics for a variety of concentrates. Viscosity must be characterized for each concentrate, unless the accuracy needed for viscosity estimations is only order of magnitude, in which case rough estimates could be made from the data in Figure 3.3-4.

4. COMBUSTION BEHAVIOR OF THE CONCENTRATES

To determine what type of thermal destruction device might be used on a commercial scale, it is necessary to know some of the general combustion characteristics of the concentrates. Some of the characteristics of greatest interest are: (1) the burning rates and the time required for complete oxidation of the combustibles; (2) the fate of the chlorine during combustion; and, (3) the ash characteristics, such as melting temperature and chemical composition.

Since the UF concentrates are more desirable as a fuel due to higher heating values and lower inorganics levels than RO concentrates, the data on combustion behavior presented in this section have been obtained for UF concentrates only.

4.1 Burning Rates

Nonisothermal (TGA) Data

The concentrates were analyzed using thermogravimetric analysis (TGA). The TGA technique determines the change in sample weight as a function of temperature and time. A small quantity of sample (less than 1 g) was placed in an inert (alumina) container connected to a micro-balance. The sample container was suspended in a furnace chamber where conditions of gas composition and temperature were controlled. The temperature was ramped

from room temperature up to 1200 °C at a rate of 20 °C per minute. The atmosphere was inert (argon) for heating from room temperature to 700 °C, and air for heating from 800 °C to 1200 °C. This was done to learn the extent of pyrolysis products in the absence of oxygen. The micro-balance recorded the loss in weight of the sample as the heating took place. The resulting mass-change versus temperature curves are shown in Figure 4.1-1.

In each case the sample showed a small mass loss at temperatures of 100 °C and less. This is undoubtedly due to a small amount of water being driven off. Though the samples were oven dried at 105 °C, they may have absorbed some water during sample handling.

The mass loss at temperatures below 700 °C is primarily due to the evolution of compounds during pyrolysis. The volatiles content varied from 38 to 60% of the original dried solids. The volatiles contents were higher for the C/D concentrates than for the E1 concentrates. Yet the E1 concentrates contained higher levels of carbon than the C/D concentrates (42-48% compared to 33-34%, see Table 3.2-5). This indicates that the E1 concentrates contained more non-volatile (i.e., char) carbon than the C/D concentrates. Thus, under pyrolysis conditions of 200-600 °C mass loss will occur at a greater rate for C/D concentrates.

The mass loss at temperatures above 700 °C is due primarily to heterogeneous oxidation of the remaining char carbon by oxygen in the air. Oxygen diffuses to the char surface and reactions occur with the char carbon producing CO and CO_2 which diffuse away from the char surface.

Not all of the mass loss at temperatures above 700 °C can be accounted for by char combustion reactions. These concentrates contain 16-19 weight % of inorganic Na and Cl, with lesser amounts of Ca and Mg. Yet at 1200 °C, mass loss levels were as great as 96%. It is evident that some vaporization of inorganics is occurring at these higher temperatures. However, the boiling points of NaCl, $CaCl_2$, and $MgCl_2$ are 1413 °C, above 1600 °C, and 1412 °C, respectively, all well above the highest TGA temperature of 1200 °C.

It is not likely that direct vaporization of these inorganic chlorides is responsible for the inorganics mass loss. A more likely explanation is that offered by Cameron (1987) for fuming during black liquor combustion. Cameron postulated that elemental sodium (boiling point 880 °C) is formed by reactions in the liquid melt phase. As elemental sodium is vaporized it reacts quickly with oxidizing species in the gas phase which produces a sodium sink enhancing the rate of sodium vaporization.

An attempt was made to determine first-order kinetic rate constants for devolatilization and char burning from the TGA curves of Figure 4.1-1. This was done by reading values of slope (-dm/dt) at various temperatures and

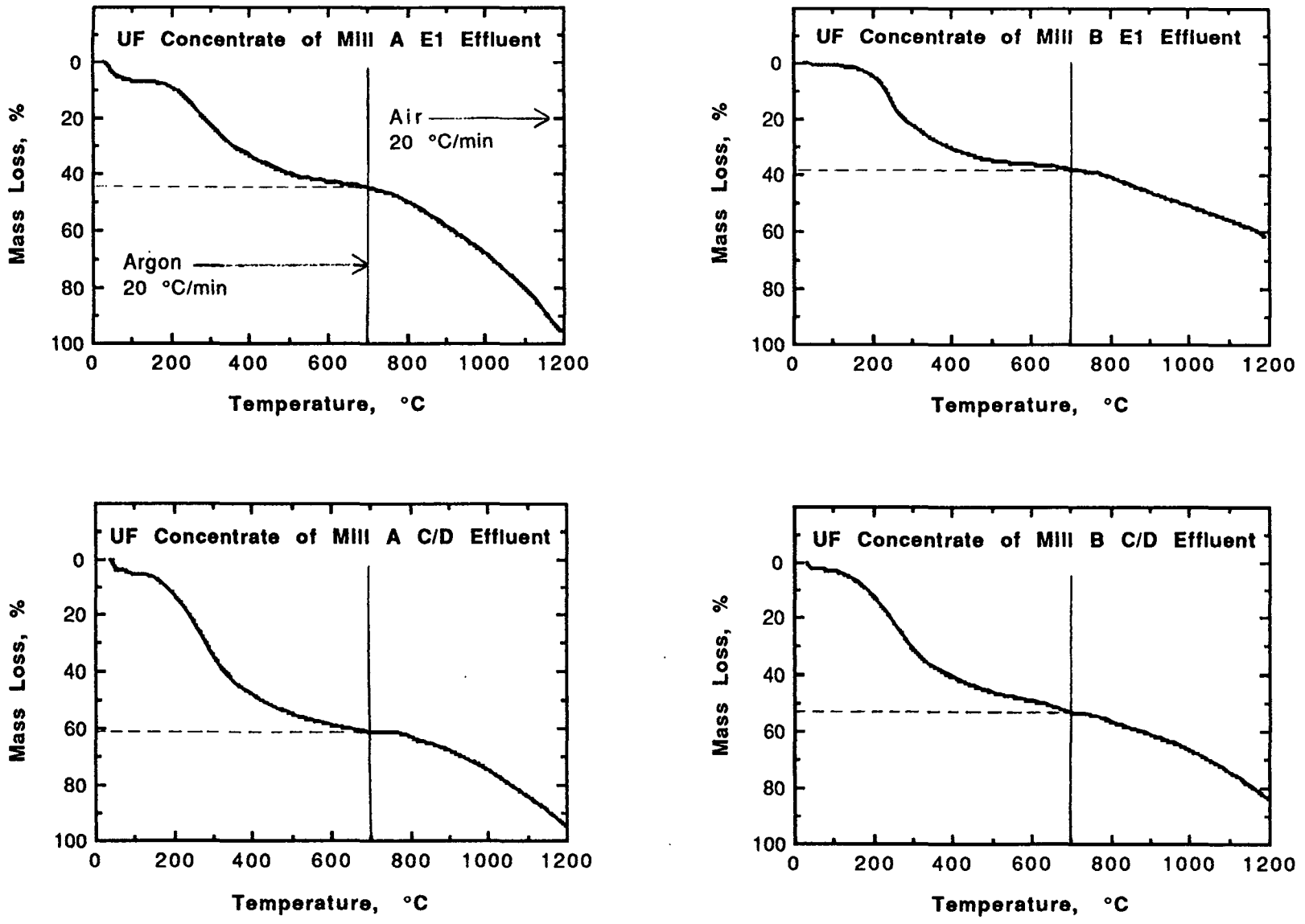

Figure 4.1-1. Nonisothermal TGA curves of UF concentrates, 20 °C/min heating rate.

then making sophisticated corrections to these slopes for nonisothermal effects. The values obtained for rate constants were unexplainably low, and it was concluded that kinetic parameters could not be derived from the TGA data.

Both Wendlant (1986) and Arnold, et al. (1979) have discussed the limitations of using nonisothermal thermogravimetry methods to study the kinetics of heterogeneous thermal decomposition reactions. On the basis of many experiments and theoretical considerations, Arnold, et al. (1979) showed that TGA curves are strongly influenced by the experimental conditions, and they concluded that the kinetic parameters calculated from these curves are fictitious and their determination is uncertain.

Isothermal Rate Data

Burning rates were obtained for one of the UF concentrates by heating small quantities (approximately 50 mg) of moisture-free concentrate in air in an electrically heated muffle furnace at 700 and 800 °C for various periods of time up to 10 minutes. During heating, the concentrate sample was contained in a small fused quartz crucible to minimize interfering reactions with the container. The floor of the crucible was a fritted piece which allowed air to circulate (percolate) through the sample during heating. The residue remaining was weighed and compared with the initial weight to determine mass loss.

The results are shown in Figure 4.1-2 where the combustible mass is on a dry and inorganic ash-free basis. The ash content for this concentrate sample was 27 weight % of the solids (see section 4.3 for determination of ash content). Each isothermal mass loss curve shows a very rapid rate of mass loss initially corresponding to volatiles evolution. This is followed by a less rapid rate of mass loss corresponding to heterogeneous char burning. Assuming that the mass loss due to char burning is negligible over the relatively short time period of devolatilization, the initial slope of the curve can be used to estimate a first-order rate constant for devolatilization,

$$k_v = -(dm_v/dt)_i/m_{v,i} \qquad \text{(eqn 4.1-1)}$$

where m_v is the mass fraction of volatiles and $-dm_v/dt$ is the rate of volatiles mass loss with respect to time, t. The subscript i denotes initial conditions at the onset of devolatilization. The initial devolatilization rate is estimated by the initial slope of the curve, at time zero. The value for $m_{v,i}$ was taken from the TGA curve of Figure 4.1-1 as 0.52 (i.e., 52% of the dry ash-free mass was volatiles). The resulting k_v values at 700 and 800 °C are shown in Table 4.1-1.

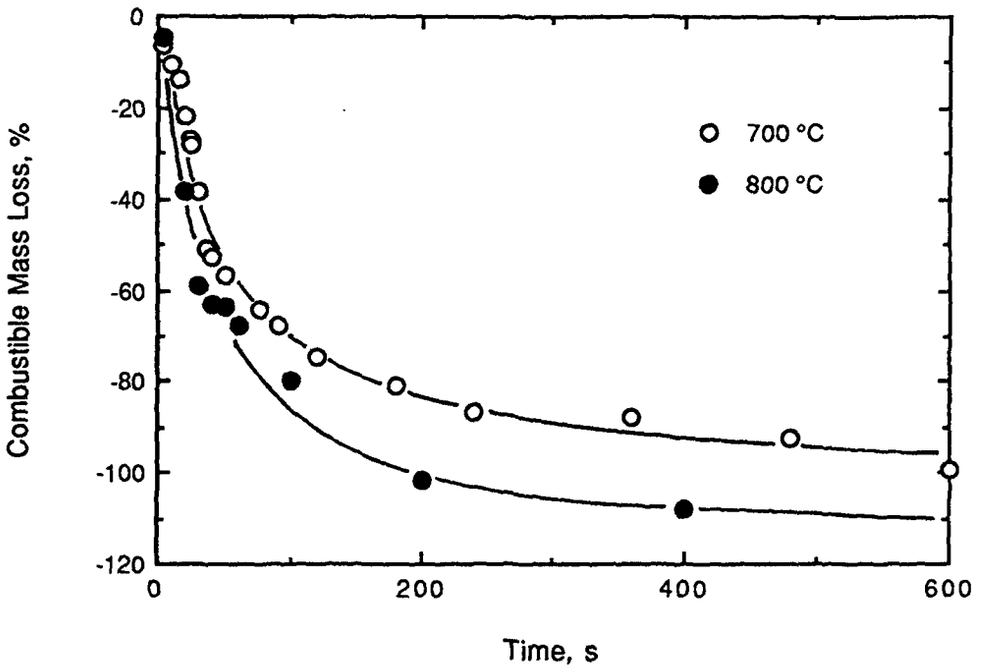

Figure 4.1-2. Isothermal mass loss curves, UF concentrate of E1 effluent (Mill B), 700 °C and 800 °C in air.

Similarly, an estimate of the first-order rate constant for char burning in air is

$$k_c = -(dm_c/dt)_i / m_{c,i} \qquad \text{(eqn 4.1-2)}$$

where m_c is the mass fraction of char and $-dm_c/dt$ is the rate of char mass loss with respect to time, t. The subscript i denotes initial conditions at the onset of char burning. The initial char burning rate was estimated by the slope of the mass loss curve at the point where devolatilization is finished (i.e., the slope at 52% combustibles mass loss). This is based on the assumption that at this point the volatiles are completely evolved and the mass loss is attributable only to char burning. The value for $m_{c,i}$ was taken as the difference between the devolatilization mass loss (52%), and the total mass loss at long heating times. Values of mc,i were 0.48 and 0.56 for 700 and 800 °C respectively. The reason for the combustible mass loss to exceed 100% at 800 °C and heating times over 200 seconds is undoubtedly vaporization of a certain amount of the inorganic ash content. The resulting k_c values at 700 and 800 °C are shown in Table 4.1-1.

Table 4.1-1. Observed First-Order Rate Constants for Burning Ultrafiltration Concentrates of E1 Effluent (Mill B)

	700 °C	800°C	
k_v, s^{-1}	2.88×10^{-2}	4.62×10^{-2}	
k_c, s^{-1}	4.79×10^{-3}	1.14×10^{-2}	
$k_v = A_v \exp(-E_v/RT)$	$A_v = 4.96\ s^{-1}$		$E_v = 9.96$ kcal/gmol
$k_c = A_c \exp(-E_c/RT)$	$A_c = 52.6\ s^{-1}$		$E_c = 18.0$ kcal/gmol

The estimation of these first-order rate constants is based on the assumption that the loss of char mass during devolatilization is negligible. The validity of this assumption is checked by comparing the TGA devolatilization curves for air and argon, as in Figure 4.1-3. At 700 °C the mass loss in air is only a small amount (2-3% of the initial mass) greater than the mass loss in argon. Thus, at 700 °C, the char mass loss during devolatilization is no more than 0.02-0.03 mass fraction. Similar measurements are not available to estimate this char mass loss during devolatilization at 800 °C.

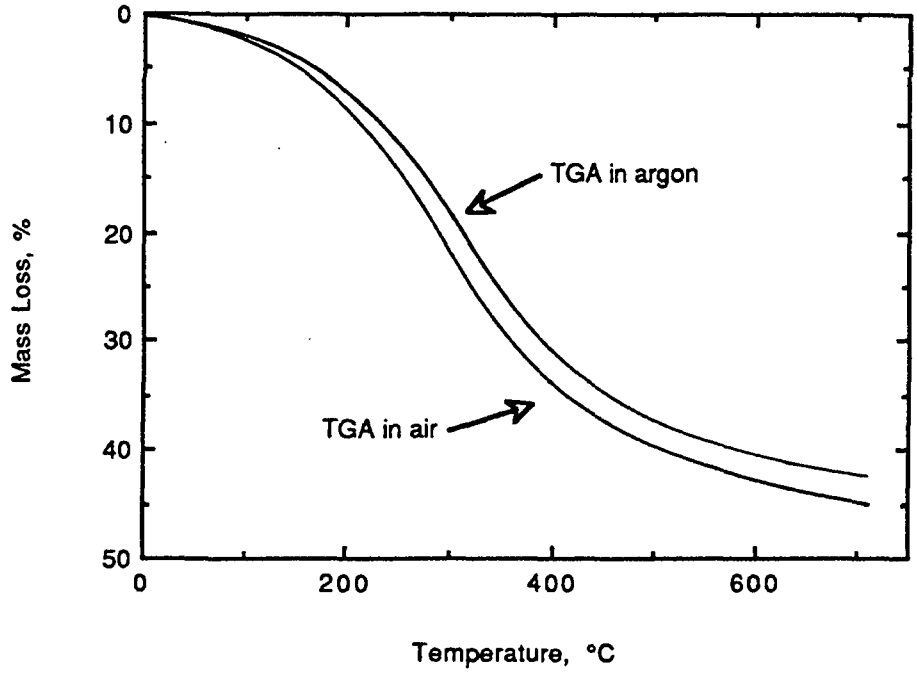

Figure 4.1-3. Devolatilization mass loss in air and in argon, UF concentrate of E1 effluent (Mill A), 20 °C/min heating rate.

With the rate constants of Table 4.1-1 the solid lines in Figure 4.1-2 were calculated from

$$m = (m_v + m_c) = m_{v,i}\exp(-k_v t) + m_{c,i}\exp(-k_c t) \qquad \text{(eqn 4.1-3)}$$

where m is the combustibles mass fraction (dry ash-free) remaining. The exponential expressions for m_v and m_c were obtained by separation and integration of Equations 4.1-1 and 4.1-2.

As seen in Figure 4.1-2, the mass loss predicted by Equation 4.1-3 follows the data very well. This shows that the estimates of first-order rate constants are accurate, and that devolatilization and char burning rates are first order with respect to concentration of volatiles and char mass.

From knowledge of the rate constants at two temperatures, values were determined for activation energies by plotting natural logarithm of rate constant versus reciprocal temperature. These activation energies, shown in Table 4.1-1, indicate that at 700 °C the rate of devolatilization doubles with a temperature rise of 150 °C, and the rate of char burning doubles with a temperature rise of 80 °C .

4.2 Fate of Chlorine

As shown in previous sections, the chemical composition of closed cycle concentrates is similar to that of black liquors, with the exception of chlorine content. The closed cycle concentrates contain high levels of chlorine as inorganic chloride and as chlorinated organics. In combusting fuels which contain significant levels of chlorine there is potential for emission of chlorinated organics in the solid and gas phase combustion products. Trace levels of chlorinated organics including ppb and ppt levels of polychlorinated dibenzodioxins (PCDD) and polychlorinated dibenzofurans (PCDF) have been measured in the gas and solid emissions of a wide variety of waste incineration facilities (Lustenhouwer, et al. 1980; Seeker, et al. 1987). This has resulted in a high level of public awareness and concern related to combustion of chlorine-containing fuels.

Chlorine Trapping by Alkali Metals

Isothermal mass loss measurements were used to determine the fate of the chlorine in burning of UF concentrates. The same procedure was used for heat treatment of small (50 mg) samples as described in section 4.1 for isothermal rate data measurement. The residue remaining after heating was dissolved in a known volume of water and the AOX concentration determined for this solution was used as a direct measure of the amount of organic chlorine in the residue. Similarly, the chloride concentration was

determined for the solution and used as a direct measure for the amount of inorganic chlorine in the residue. The sum of organic chlorine and inorganic chlorine was considered as the total chlorine. The results are shown in Figure 4.2-1 for one of the UF concentrates of E1 effluent.

As the sample was heated, the amount of organic chlorine decreased sharply, mirrored by an increase in inorganic chlorine, such that the total chlorine mass in the unburned residue remained relatively constant. Thus, heating caused a significant decrease in the chlorinated organics but did not result in the loss of significant chlorine to the vapor phase. Rather, the chlorine was tied up as metal chlorides, primarily NaCl, based on the high levels of sodium present (refer to Table 3.2-5). This is a significant result because of the implication for emission of trace levels of PCDD/PCDF and similar chlorinated organic compounds during burning of concentrates. This would seem to imply that burning of chlorine-containing concentrates would not pose a serious potential for PCDD/PCDF emissions as long as the concentrate contained more moles of Na than Cl.

The trend in total chlorine shown in Figure 4.2-1 does not appear to be physically possible; it shows the mass of total chlorine to be increasing at heating times of greater than 25 seconds. There is no reason to expect that gasified chlorine would return to the solid residue. Any chlorine gasified would have been carried away by air percolating through the sample and by pyrolysis gases leaving the sample, and would have had no opportunity to return to the solid residue. A plausible explanation for the data trend is that AOX is a less than perfect indicator of organic chlorine in the unburned residue, and that the AOX mass found in the residue containing solution was less than the true mass of chlorinated organics. This is supported by the observation that the mass of total chlorine in the residue approaches the initial mass of total chlorine as time increases. As time increases, the total chlorine value becomes less and less dependent on the AOX value.

Chlorine trapping was also observed by Sasaki, et al. (1983) in their study of pyrolysis behavior of chlorinated thiolignin and organic matter isolated from spent alkali-extraction liquor. Essentially all (99.1 weight %) of the total chlorine from spent alkali extraction liquor was found in the solid residue after pyrolysis at 720 °C in N_2. Upon pyrolysis of chlorinated thiolignin (containing no alkali) at 710 °C in N_2, 90% of the total chlorine was recovered as HCl, 5-10% as methyl chloride, and 2-5% remained in the solid residue. With alkali addition this chlorine distribution was remarkably changed; the chlorine content in the solid residue increased to 99% with increase in alkali to a Na/Cl molar ratio of 1.0.

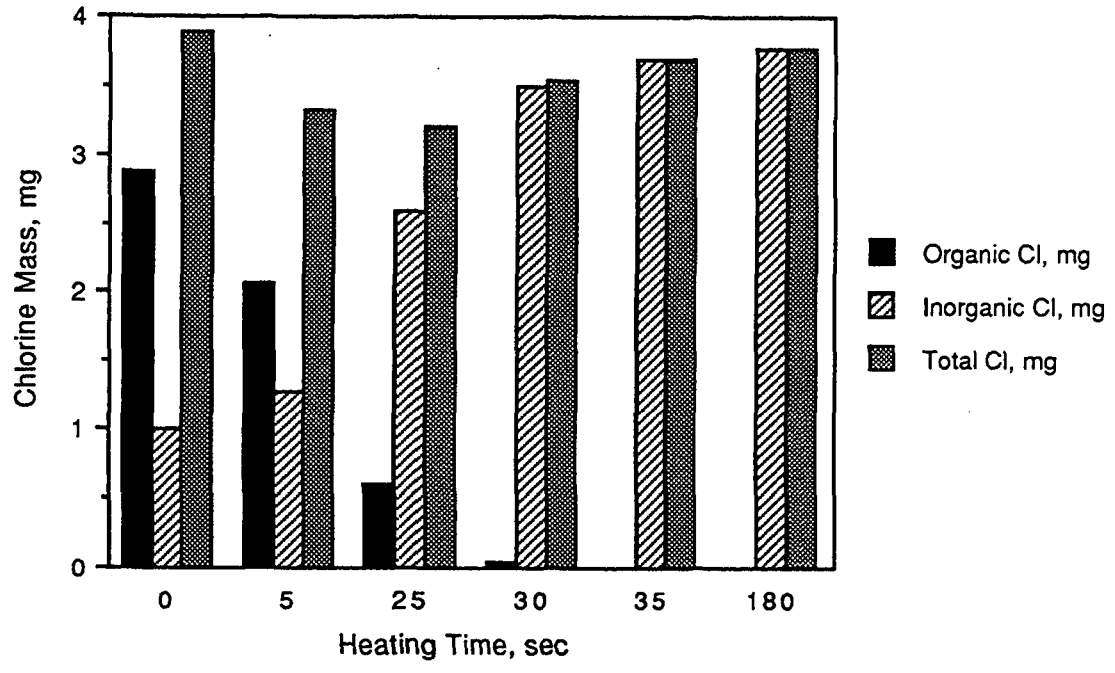

Figure 4.2-1. Trapping of chlorine during heating of UF concentrate of E1 effluent (Mill B), 700 °C in air.

Thermal Stability of Chlorinated Organics

The thermal stability of chlorinated organics in the concentrate is compared to the thermal stability of the total combustible mass in Figure 4.2-2. There are two data sets; one results from using AOX values for organic chlorine, and the other results from using chloride values for organic chlorine. In the latter case it is assumed that total chlorine in the residue remains constant. With this assumption, the organic chlorine is found by subtraction of the inorganic chlorine mass from the total chlorine mass.

It is clear that the concentration of chlorine-containing organics decreased at a rate 2-5 times faster than the rate of destruction of total organics (as evidenced by comparing the initial slopes in Figure 4.2-2). It is also evident that 90% or more of the organic chlorine trapping occurred before 50% loss in combustible mass had occurred. Since 52% of the combustible mass was volatiles, this provides evidence that the trapping occurred during pyrolysis. This is consistent with the finding of Sasaki, et al. (1983) that 99.1% of the chlorine was trapped in the solid residue during pyrolysis of organic material from spent alkali-extraction liquor.

Chemical Equilibrium Predictions

Thermodynamic equilibrium calculations were used to predict the fate of chlorine for various levels of Na in the fuel. The predictions, shown in Figure 4.2-3, show a trend similar to that observed both in this study and in the study of Sasaki, et al. (1983). With no Na present, chemical equilibrium predicted that nearly all of the chlorine is present as HCl, with small amounts of Cl_2 (not shown in Figure 4.3-3). As Na was added and the molar ratio of Na/Cl increased, the equilibrium concentration of HCl decreased and was mirrored by a commensurate increase in NaCl concentration. At Na/Cl molar ratios above 1.5, essentially all of the chlorine was predicted to be trapped as NaCl.

These equilibrium predictions were made using CET86, a code developed by Gordon and McBride (1976) at the NASA Lewis Research Center for prediction of complex chemical equilibrium compositions. The code contains thermodynamic data for a large number of compounds (over 3,000). Input is the moles of C, H, O, Na, Cl, and S in the fuel (concentrate), moles of O and N in the oxidizer (air), initial energy state (heat of formation at 298 K) for fuel and oxidizer, and pressure. The code performs a minimization of the Gibbs free energy to give the composition of products which yields the lowest free energy state. The calculation was performed under adiabatic conditions, that is, the energy released in converting the fuel and oxidizer to reactants was assumed to be used solely for heating the predicted products. The level of oxidizer was 20% excess air, the starting temperature of the fuel and oxidizer

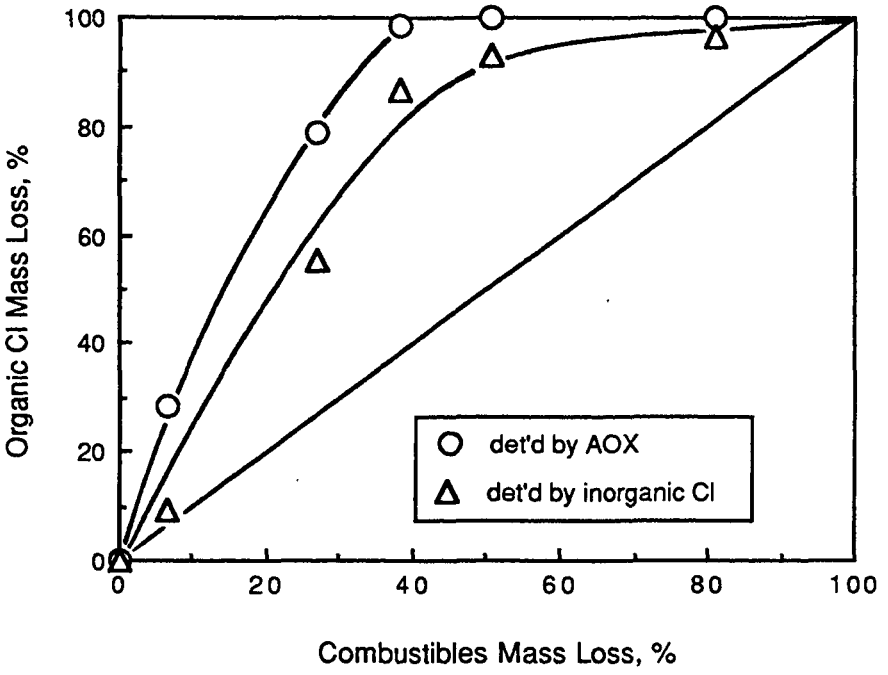

Figure 4.2-2. Relative thermal stability of chlorinated organics in UF concentrate of E1 effluent (Mill B), heating times of 5, 25, 30, 35, 180 s, 700 °C in air.

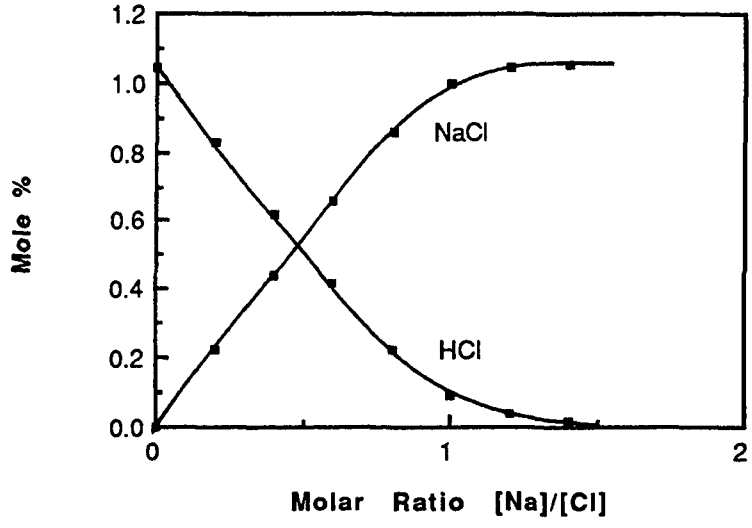

Figure 4.2-3. Prediction of fate of chlorine based on chemical equilibrium.

was 298 K, and the moisture-free chemical composition of UF concentrate of E1 effluent from Mill B was used as input. The adiabatic flame temperature thus predicted was approximately 2000 K.

4.3 Ash Characteristics

The term ash is used to denote that portion of the concentrate sample which remains as solid residue after the sample is heated in air at 750 °C until no further weight loss occurs. The definition of ash is somewhat arbitrary in that it depends on the ashing temperature, a higher temperature giving lower ash values. Ash consists primarily of the inorganic metals and metal compounds in the concentrates which have relatively high melting points and low volatilities compared to the organic compounds. Ash samples from all eight concentrates were analyzed for fusion (melting) temperature and composition. The results are shown in Table 4.3-1.

Table 4.3-1. Characteristics of Concentrate Ashes

	Mill A C/D		Mill A E1		Mill B C/D		Mill B E1	
	UF	RO	UF	RO	UF	RO	UF	RO
% Ash[a]	21.9	62.5	17.2	47.8	23.3	51.9	26.6	56.0
ID, °C[b]	>1050	650	790	600	>1050	650	>700	600
FL, °C[c]	>1050	>1050	840	750	>1050	>1050	>800	750
Cl^-	45.3	35.7	51.9	45.7	31.1	33.8	28.4	40.9
Na^+	20.9	21.3	43.6	37.3	16.5	20.3	39.7	38.6
$SO_4^=$	11.5	2.0	5.1	2.5	9.2	3.7	6.9	2.7
$CO_3^=$	ND[d]	ND	0.4	2.0	ND	ND	ND	2.8
Total	77.7	59.0	101	87.5	56.8	57.8	75.0	85.0
Total (Na_2O)[e]			112	96.5			91.5	97.0
Initial Na/Cl	0.42	0.57	1.47	1.41	0.36	0.37	1.26	1.99
Ash Na/Cl	0.71	0.92	1.29	1.26	0.82	0.93	2.16	1.45
$(Na/Cl)_f/Na/Cl)_i$	1.69	1.61	0.88	0.88	1.64	2.51	0.96	0.73

a Determined by ashing solids in air @ 750 °C

b Initial deformation temperature

c Fluid Temperature

d Not detectable, <0.02%

e Assuming excess Na is present as Na_2O

The relative percentages of ash found in the dry solids ranged from 17% to 64% by weight. The RO concentrates have much higher ash content (55% avg) than the UF concentrates (22% avg). This supports the observation made earlier that UF concentrates have higher heating values and are a more desirable fuel than RO concentrates. This is due to the rejection characteristics of the membranes; the more selective UF membranes result in a less inorganic and more organic concentrate.

Estimates of the initial deformation temperatures and fluidization temperatures of the ashes were performed in a tube furnace in air. These are estimates and should not be relied upon as being precise determinations of the melting temperatures. The ashes from UF concentrates show higher initial deformation temperatures (700-790 °C) than do the ashes from RO concentrates (600-650 °C)—another reason why RO concentrates are less desirable as a fuel, especially in a fluid bed or other low temperature furnace. In such a furnace, the RO concentrates would be less likely to remain as a solid.

The compositions determined on the ash were the elements Cl, Na, S (as sulfate), and C (as carbonate). Very little carbonate was found in any of the ashes. The Cl and Na content accounted for the majority of the ash weight, with the sulfate being next largest in concentration. The amounts and relative proportions of Na and Cl in the ash suggest that the majority of the ash is NaCl. Certainly there is some Na_2SO_4 present, and probably some $MgCl_2$ and $CaCl_2$ as well.

The molar Na/Cl ratios show an excess of Na for E1 ashes and an excess of Cl for C/D ashes. The initial Na/Cl molar ratios for the concentrate solids (from Table 3.2-5) are included for comparison. For all four C/D concentrates, the Na/Cl molar ratio increased during heating in air by an average factor of 1.9—evidence that significant chlorine was gasified. This is consistent with the discussion on chlorine trapping by alkali, since the C/D concentrates did not contain enough Na to trap the Cl. For all four E1 concentrates, the Na/Cl molar ratio decreased slightly (by about 10% on average) during heating in air. It is not clearly understood why this decrease occurred. Chlorine trapping would result in an approximately constant level of chlorine. It appears that noticeable sodium vaporization occurred.

The sums of weight percentages for the compounds shown in Table 4.3-1 are less than 100% in most cases, indicating the presence of other elements in the ash. One possibility is oxygen, bound in metal oxides. Hydroxide peaks were seen in the Ion Chromatograph tests made by dissolving some of the ash in water to determine the concentration of sulfate and chloride in the water. It is known that Na_2O reacts readily with water to form NaOH, thus, the hydroxide peaks observed could be the result of Na_2O which was present in the ash. This is especially likely for the E1 concentrates which have a molar

excess of Na. Estimates were made of the mass of Na_2O in the E1 ashes by assuming that all of the excess Na was present as Na_2O. Including this estimated Na_2O, the sums of weight percentages for E1 ashes range from 92 to 112% and average 99%. It appears plausible then that essentially all of the mass is accounted for by the values in Table 4.3-1 for E1 ashes.

In the case of the C/D ashes, the fluid melting point exceeds 1050 °C This is significantly greater than the melting points of NaCl (801° C), Na_2SO_4 (884° C), $MgCl_2$ (708° C), and $CaCl_2$ (772° C). The high melting point suggests the presence of refractory compounds, such as silica compounds. No data are available to verify levels of refractory or other compounds in the C/D ashes.

5. REVIEW OF THERMAL DESTRUCTION TECHNOLOGIES

A number of thermal destruction technologies have effectively handled various waste streams. Some of these are rotary kiln incinerators, fluid bed combustors, circulating fluid bed combustors, gasification of waste to medium or low BTU fuel gas, and co-firing waste with other fuels such as black liquor, bark, coal, oil, and gas. The data presented on chemical composition, heating value, physical properties and burning rates show that as a fuel, concentrates from UF treatment of E1 effluents behave similarly to kraft black liquors. This indicates that the concentrates could feasibly be burned rapidly and effectively using one of these technologies.

Two considerations of key importance in choosing a thermal destruction method for chlorine-containing concentrates are (1) corrosion and (2) emission of chlorinated organics. With the high levels of chlorine, the melting point of the inorganic ash is lowered, and corrosion difficulties in the combustion equipment are increased. With the high levels of chlorine, potential exists for emission of chlorinated organic compounds in the flue gas.

With these considerations in mind, fluid bed combustion is perhaps the most attractive technology for thermal destruction of chlorine-containing concentrates. Fluid bed combustion is a low temperature combustion technology, capable of operating in the range 700-800 °C (below the ash fusion temperature). Maintaining the inorganic ash as a solid would greatly reduce the potential for corrosion problems. At this temperature window, high destruction efficiencies of organics in the concentrates is attainable given sufficient heating times, as evidenced by the isothermal rate data reported in the previous section. Fluid bed combustion provides a very high level of mixing of fuel with oxidizer, and relatively long residence times for the solid particles. This should make fluidized bed combustion capable of high destruction efficiencies for the organics present in concentrates. The mixing is also expected to enhance the trapping of organic bound chlorine as NaCl in

the bed material. None of the other thermal destruction technologies mentioned above would provide this low temperature capability while maintaining high organics destruction efficiency.

6. CONCLUSIONS

The main conclusions resulting from this study are:

1. Applying thermal destruction to UF concentrates of spent alkali extraction liquors is highly feasible.

2. Emission of trace levels of PCDD/PCDF and other chlorinated organics is expected to be minimal due to trapping of the organic chlorine as NaCl.

3. Fluidized bed combustion appears to be the most likely thermal destruction technology for these concentrates. It is expected that fluidized bed combustion will provide effective organics destruction at temperatures low enough to prevent melting of the inorganic (non-combustible) ash constituents.

A number of specific observations which support these conclusions are:

1. The selective nature of ultrafiltration resulted in high removal efficiencies for organics and low removal efficiencies for inorganics which yielded concentrates with low levels of non-combustible ash (22 weight % of moisture free solids).

2. Reverse osmosis resulted in high removal efficiencies for inorganics which yielded concentrates with high levels of ash (55 weight % of moisture free solids).

3. The UF/E1 concentrates were very similar to black liquor in chemical composition (excepting higher Cl content), heating value, specific gravity, and viscosity. Specific gravity values are predictable using an expression with terms for solids level and temperature. Viscosity values are not predictable and must be characterized for each individual concentrate.

4. The Cl content of UF/E1 concentrates was 8-9 weight % (of the moisture free solids), with approximately 75% of this being organically bound.

5. Upon heating UF/E1 concentrates in air at 700 and 800 °C, essentially all of the organic chlorine was trapped in the solid residue as NaCl. This trapping occurred during the relatively short time frame of devolatilization at a rate 2-5 times greater than the rate of volatiles evolution.

6. By weight, UF/E1 concentrates consist of approximately 40% volatiles, 40% char (non-volatile combustible material), and 20% non-combustible ash. The volatiles evolve rapidly in the temperature range 200-600 °C. The char reacts heterogeneously with oxygen in the air at temperatures of 600-900 °C.

7. The mass loss during burning of UF/E1 concentrates is described adequately by a two-part model, consisting of one rate expression for devolatilization which is first-order in volatiles concentration, and a second rate expression for char burning which is first-order in char concentration.

8. The non-combustible ash consists primarily of NaCl with some Na_2SO_4 and very little Na_2CO_3; it undergoes initial deformation at 700-790 °C and complete melting at 840-1050 °C.

7. RECOMMENDATIONS

Future work should be directed along two parallel paths: potential for fluid bed combustion of concentrates and potential for burning of concentrates in recovery boilers.

Fluidized bed combustion is likely a feasible thermal destruction technology for chlorine-containing concentrates, but needs to be verified experimentally. This should occur first in a laboratory-scale or small pilot-scale fluidized bed combustor where conditions of temperature, gas residence time, solids residence time, stoichiometry, and other key variables can be controlled and manipulated. Such tests should demonstrate the temperatures and residence times necessary to accomplish high levels of destruction of organics as well as high levels of chlorine trapping as NaCl. The emissions of HCl and of PCDD/PCDF and other chlorinated organics should be measured to assess the potential for emission of these compounds during fluidized bed combustion of concentrates.

Since the chemical composition, heating value, and physical properties of concentrates are similar to kraft black liquor, destroying concentrates by adding them to black liquor and burning them in a recovery furnace may be accomplished without derating the fuel value. There is the concern of adding chlorine to the recovery cycle; however, the reasonably low levels of chlorine in concentrate solids (8-9 weight %) may not result in recovery cycle chloride levels higher than those experienced routinely at coastal mills. This would be especially true if there were chloride purge points in the recovery cycle to provide sufficient chloride removal.

Therefore, the feasibility of burning concentrates with black liquor in a recovery boiler should be investigated. Important issues to be addressed are the potential for HCl emissions and for formation and emissions of chlorinated organics such as PCDD/PCDF. The potential for low temperature formation of PCDD/PCDF should also be investigated. It has been shown for municipal waste incinerators that these compounds form in low temperature regions (near 300 °C) such as in the electrostatic precipitator by the chlorination of unburned hydrocarbons on the high surface area particulate matter. Such low temperature formation is catalyzed by the presence of various metals. It seems possible that low temperature catalytic formation may occur in the electrostatic precipitator of a recovery furnace.

The potential for PCDD/PCDF emissions could be accomplished by burning small quantities of mixtures of black liquor and concentrate and using an EPA modified method 5 or other suitable sample train to adsorb the trace levels of chlorinated organics species in the off gas. The extent of low temperature PCDD/PCDF formation could be examined by heating small quantities (a few grams) of recovery boiler fly ash in air at temperatures between 100 °C and 600 °C and comparing the concentrations of trace chlorinated organics on the solid residue to those on the unheated fly ash.

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8. REFERENCES

Adams, T. N., and Frederick, W. J. *Kraft Recovery Boiler Physical and Chemical Processes.* The American Paper Institute, New York, NY (1988).

Arnold, M., et al. *J. Thermal Anal.* 17:507(1979).

Cameron, J. H. Reaction Enhanced Vaporization of Molten Salt. *Chem. Eng. Comm.* 59:243-257(1987).

Champion International Corporation. Color Removal Demonstration Report. Canton Mill, Canton, North Carolina (May 8, 1986).

Dorica, J. Ultrafiltration of Bleach Plant Effluents-A Pilot Plant Study. *Journal of Pulp and Paper Science.* 12(6):J172(November, 1986).

Dorica, J., Wong, A., and Garner, B. C. Complete Effluent Recycling in the Bleach Plant with Ultrafiltration and Reverse Osmosis. *Tappi Journal.* p. 122(May, 1986).

Fricke, A. L. Physical Properties of Kraft Black Liquor. Summary Report-Phases I and II, Report DOE/CE/40606-T5 (DE88002991). (September, 1987).

Gordon, S. and McBride, B. J. Computer Program for Calculation of Complex Chemical Equilibrium Compositions, Rocket Performance, Incident and Reflected Shocks, and Chapman-Jouguet Detonations. NASA SP-273 (1976).

Lundahl, H., and Mansson, I. Ultrafiltration for Removing Color from Bleach Plant Effluent. *Tappi Journal.* 63(4):97(April, 1980).

Lustenhouwer, J. W. A., Olie, K., and Hutzinger, O. Chlorinated Dibenzo-p-Dioxins and Related Compounds in Incinerator Effluent: a Review of Measurements and Mechanisms of Formation. *Chemosphere.* 9:501-22 (1980).

Regestad, S. O., *Svensk Papperstidning*, 54(2): 36 (1951).

Reid, W. T., et al. Heat Generation and Transport, section 9 of *Chemical Engineers' Handbook.* Perry, R. H., and Chilton, C. H., editors, 5th edition, McGraw-Hill, New York, NY (1973).

Sasaki, N., et al. Pyrolysis and Combustion Behavior of Chlorinated Organics in Bleach Plant Effluent. Int. Symp. Wood & Pulping Chem., Japan. 3: 150-155 (May 23-27, 1983).

Seeker, W. R., Lanier, W. S., and Heap, M. P. Municipal Waste Combustion Study: Combustion Control of MSW Combustors to Minimize Emission of Trace Organics. Final Report EPA/530-SW-87-021c, EPA Contract 68-02-4247, prepared for James Kilgroe, Air and Energy Engineering Research, U.S. Environmental Protection Agency, Research Triangle Park, NC (May, 1987).

Seeker, W. R., et al. The Thermal Decomposition of Pulverized Coal Particles Eighteenth Symposium (International) on Combustion. The Combustion Institute, Pittsburgh, PA, p. 1213 (1981).

Venkatesh, V., and Nguyen, X. N. Evaporation and Concentration of Black Liquor, chapter 3 of *Chemical Recovery in the Alkaline Pulping Processes,* Hough, G., editor, Tappi Press, Atlanta, GA (1985).

Wendlant, W. W. *Thermal Analysis,* 3rd Edition, Wiley-Interscience, New York (1986).

Wolf, A. V., et al. Concentrative Properties of Aqueous Solutions: Conversion Tables, in Section D of *Handbook of Chemistry and Physics,* 67th Edition, Weast, R. C., et al., editors, CRC Press, Boca Raton, Florida (1974).